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VII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

BROMINE DERIVATIVES OF METAPHENYLENE DIAMINE.

By C. Loring Jackson and Sidney Calvert.

Presented May 9, 1894.

Introduction.

In the course of an extended investigation of the behavior of the tribromdinitrobenzol melting at 192°, carried on now for some years in this laboratory, we took up the reduction of this substance with tin and hydrochloric acid, since, if the bromine was not removed, new bromine derivatives of metaphenylene diamine must be obtained, or, on the other hand, the replacement of the bromine by hydrogen would be of interest, because cases in which a halogen is removed from the benzol ring under these conditions, are far from common. As, however, two of those already observed had occurred in the work on derivatives of tribromdinitrobenzol done in this laboratory, we had reason to hope that the proposed experiments might furnish us with an additional case, and contribute something toward determining the conditions under which this replacement of bromine by hydrogen takes place. After we had begun our work there appeared a paper * by Schlieper on the removal of bromine from aromatic compounds by tin and hydrochloric acid, in which he announced his intention of making an extended research in this field; we accordingly wrote to Victor Meyer, under whose direction Schlieper was working, asking if we might finish our work, and he has with great courtesy given us permission to do so.

We have succeeded in finding only the following cases in which bromine is replaced by hydrogen in aromatic compounds by reduction with tin and hydrochloric acid. Unsymmetrical brommetadinitrobenzol gives metaphenylene diamine.† Tribromdinitrobenzol sulphonic acid

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* Ber. d. ch. G. XXV. 552.

† Zincke and Sintenis. Ber. d. ch. G., V. 792.

gives bromdiamidobenzolsulphonic acid.[*] Dibromdinitrophenylmalonic ester gives bromamidoxindol,[†] nitrite of bromdinitrophenylmalonic ester gives amidoxyoxindol.[‡] Bromnitrophenol gives amidophenol, and bromnitranisol gives amidoanisol.[§] Metabromorthonitrobenzoic acid and its isomeric form both give anthranilic acid,[||] and Hübner[¶] also states that he obtained small quantities of orthophenylene diamine from nitroparabromaniline, but that the principal product was the bromphenylene diamine ; this, however, seems to be the only case observed, and none are recorded to our knowledge in the para series. We could find no record of the removal of other halogens under these conditions, until Schlieper published a second paper [**] (after our work on tribromdinitrobenzol was finished), in which he describes the reduction of chlor- and iodnitrophenols or anisols, when he found that iodine was removed just as bromine was, but that chlorine was not replaced by hydrogen. On the other hand he found that bromine could not be removed from derivatives of ortho- or paranitrophenols, as was to be expected from the work of previous observers. From his experiments he infers that bromine or iodine is replaced by hydrogen under the influence of tin and hydrochloric acid, when it stands in the ortho position to the two negative groups (OH. Br. NO_2. 1, 2, 3), although he has not yet succeeded in bringing an absolute proof that this is the constitution of the substances with which he worked.

Our experiments proved that when tribromdinitrobenzol was treated with a mixture of tin, hydrochloric acid, and a little alcohol,[††] all three of the atoms of bromine were replaced by hydrogen, the product being metaphenylene diamine. Schlieper's inference given in the preceding paragraph, therefore, is not of general application, as, if this were the case, only one atom of bromine would have been removed from the tribromdinitrobenzol, since only one of them is in the ortho position to both of the nitro groups, the constitution of this substance being Br. NO_2. Br. NO_2. Br. H. It is to be observed also that the conversion of unsymmetrical brommetadinitrobenzol into metaphenylene diamine, observed by Zincke and Sintenis, is not in harmony with this inference of Schlieper. Although, therefore, the diortho position is not essential to the removal of bromine by tin and hydrochloric acid, there is no doubt that Schlieper is right in considering it the most favorable position for this purpose, as the replacement by hydrogen of an atom of bromine standing between two nitro groups has been repeatedly observed in this laboratory with comparatively weak reducing agents, such as sodium malonic ester, and probably sodium acetacetic ester, or sodic ethylate.

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[*] Baessmann, Ann. Chem. CXCI. 244.

[†] Jackson and Bancroft, these Proceedings, XXIV. 299.

[‡] Jackson and Bentley, these Proceedings, XXVI. 95.

[§] Schlieper Ber. d. ch. G., 1892, p. 552.

[||] Hübner Petermann, Ann. Chem. CXLIX. 135.

[¶] Ann. Chem. CCIX. 360.

[**] Ber. d. ch. G., XXVI. 2465.

[††] Schlieper used stannous chloride and hydrochloric acid in his work, and it is possible that this difference may have modified the result.

In trying to find the cause of the replacement of all three atoms of bromine by hydrogen in the reduction of tribromdinitrobenzol the most obvious theory was that the attachment of the atoms of bromine to the benzol ring was weakened by the presence of the two negative nitro groups, as is so frequently observed in other reactions. If this was the case, the bromine would be removed before the nitro groups were reduced, and tribromphenylene diamine would not lose its bromine on treatment with tin and hydrochloric acid. Upon trying this experiment, however, we found that the whole of the bromine was removed from the tribromdiamine as easily as from tribromdinitrobenzol.* It follows, therefore, that the nitro groups are not the cause of the easy removal of the three atoms of bromine in the reduction of tribromdinitrobenzol. A parallel experiment with dibromphenylene diamine showed that this substance gave up its bromine with much more difficulty than the corresponding tribrom compound, for whereas the tribrom derivative was converted into phenylene diamine in a few minutes, it took over twelve hours to bring about the same change in the dibrom compound. It is evident from these unexpected results that the removal of the bromine atoms depends in part upon their position toward each other, and this is not strange, as in other cases it has been observed that three bromine atoms, when in the symmetrical position on a benzol ring, are more loosely attached than two in the meta position; but this is not the only cause of their removal, since symmetrical tribrombenzol is not reduced by tin and hydrochloric acid. It would seem, therefore, that the replacement of these atoms of bromine is caused principally by the fact that there are other radicals attached to the ring, with little regard to the nature of these radicals, as the highly positive amido groups apparently produce the same effect as the highly negative nitro radicals. An additional argument for this conclusion was furnished by experiments on the reduction of tribromaniline which was converted into dibromaniline by the action of tin and hydrochloric acid for a few hours. From the facts at present known we are unable to deduce any rule in regard to the position which these other radicals must occupy in order to cause the replacement of bromine by hydrogen, when the compound is treated with tin and hydrochloric acid.

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* Other reagents, for instance sodic ethylate or sodic hydrate, do not remove bromine from the diamine.

After we had found, as just described, that the bromine was removed by the action of tin and hydrochloric acid upon tribromdinitrobenzol, we turned our attention to the study of the bromine derivatives of metaphenylene diamine, as only one of these had been described, — a dibromphenylene diamine, which Hollemann * stated he had obtained by the action of bromine water on the chloride of phenylene diamine. He gives, however, neither melting point nor analysis of his substance. Upon trying to repeat his preparation we found that bromine water converted the chloride of phenylene diamine (or the free base suspended in water) into a tribromphenylene diamine melting at 158°. As the product is the same, when an insufficient quantity of bromine is used, a portion of the phenylene diamine remaining unaltered in this case, the statement of Hollemann must have rested on an error of observation. A paper by Vaubel,† which appeared after our work on this subject was finished, confirms our result, as he found by a volumetric method that three atoms of bromine are substituted for hydrogen in the molecule of phenylene diamine, when it is treated with a mixture of potassic bromide, sulphuric acid, and potassic bromate. We have made the same tribromphenylene diamine by the action of zinc dust and acetic acid on the tribromdinitrobenzol; this method of preparation proves that its constitution is $Br. NH_2. Br. NH_2. Br. H$.

A dibromphenylene diamine can be obtained by the action of bromine in excess upon phenylene diacetamide. The dibromphenylene diacetamide melts at 259° to 260° ; the free base at 135°. We have not succeeded in determining the constitution of this dibromphenylene diamine. Nor have we obtained the corresponding monobromphenylene diamine. A monobromphenylene diamine belonging to another series was obtained, however, by reducing tetrabromdinitrobenzol melting point 227° with tin and hydrochloric acid; it melts at 93°–94°, and from our experiments on the reduction of tribromdinitrobenzol there can be little doubt that it has the symmetrical constitution $Br. H. NH_2. H. NH_2. H$. When treated with bromine three atoms are sub-

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* Zeitschr. f. Chem. 1865, p. 555.

† Journ. Prakt. Chem. [2] XLVIII. 75.

stituted for three of hydrogen in its molecule, and the tetrabromphenylene diamine is formed, which melts at 212°–213°.

The presence of the bromine in the molecule of metaphenylene diamine has a strong effect on its tendency to form salts and on the composition of the salts formed. The tetrabrom and tribrom compounds do not form salts under ordinary conditions, but tribromphenylene diamine can be converted into its chloride by passing hydrochloric acid through a solution of it in benzol; this salt, however, gives up part of its hydrochloric acid at ordinary temperatures, the whole of it at 100°. The dibromphenylene diamine, on the other hand, forms salts more easily, and its chloride is only partially decomposed at 100°, while the bromide of this base seems to be even more stable. All three of these salts contain but one molecule of the acid, the chloride of dibromphenylene diamine, for example, having the following formula $C_6H_2Br_2NH_3ClNH_2$. The monobromphenylene diamine forms salts still more easily, and they are also more stable. The bromide contains two molecules of hydrobromic acid having the formula $C_6H_3Br(NH_3Br)_2$. We have also prepared the tribromphenylene diacetamide, which does not melt at 330°, and the tribromphenylene diurethane melting at 212.°

Experimental Part.

Tribrommetaphenylene Diamine $C_6HBr_3(NH_2)_2$.

The most convenient method for preparing this substance consists in passing a stream of air and bromine vapor into a solution containing metaphenylene diamine, for instance that obtained by adding sodic hydrate or carbonate to the product of the reduction of metadinitrobenzol with tin and hydrochloric acid until all the tin is precipitated and filtering out the hydrate of tin. In adding the bromine an excess must be avoided, as this turns the product black, and we have therefore found it well to filter the precipitate out by means of cheese-cloth as fast as a sufficient quantity of it was formed, continuing the action of the bromine vapor on the successive filtrates as long as a precipitate appeared. The crude product, which was always dark colored, was dried, and then crystallized from alcohol containing a little benzol until it showed the constant melting point 158°, when it was dried at 100° and analyzed with the following results:—

I. 0.1459 gram of the substance gave by the method of Carius 0.2392 gram of argentic bromide.

II. 0.2022 gram of the substance gave 14.65c.c. of nitrogen at a temperature of 19° and a pressure of 771.9 mm.

	Calculated for $C_6HBr_3(NH_2)_2$.	Found. I.	Found. II.
Bromine	69.56	69.78	
Nitrogen	8.11		8.21

These analyses prove that the substance is tribromphenylene diamine, and therefore our experimental result does not agree with that of Hollemann,* who stated that he obtained a dibromphenylene diamine by the action of bromine water on a solution of the chloride of phenylene diamine. As it was possible that this difference in the results of the action might be due to the fact that Hollemann used a salt of phenylene diamine, whereas we used in our first experiments the free base dissolved and suspended in water, we repeated our experiment with a solution of the chloride of phenylene diamine, and obtained precisely the same result as with the free base, that is, the tribromphenylene diamine melting at 158°. We are therefore forced to the conclusion that Hollemann's statement is due to an error in observation.

Properties. Tribromphenylene diamine crystallized from alcohol appears in long slender needles united longitudinally into ribbons with the ends serrated so strongly that they look like combs. It is white, with marked silky lustre, and melts at 158°. It is not very soluble in cold but freely in hot alcohol; somewhat more soluble in methyl than ethyl alcohol; freely soluble in acetone; soluble in ether, benzol, chloroform, glacial acetic acid, or carbonic disulphide; very slightly soluble in ligroine, but good crystals may be obtained from its solution in hot ligroine; essentially insoluble in water. Strong hydrochloric acid dissolves it easily in the cold, depositing after long standing white transparent crystals which soon turn brown; on heating the solution in hydrochloric acid it turned dark brown, almost black, showing decomposition of the substance; the formation of a similar nearly black decomposition product was brought about at once by cold strong nitric acid. Cold strong sulphuric acid dissolved the tribromphenylene diamine at once, the solution having a purplish tint, which turned to dark brown if it was allowed to stand for some time, or if it was stirred in a current of air for a short time. Nevertheless on one occasion a white solid was obtained, but before it could be collected a black spot appeared in one part of it which sped rapidly through the whole mass. Dilute sulphuric acid had no apparent effect on it in the cold, but decomposed it when hot. These observations show that the presence of the three atoms of bromine has destroyed in great measure the basic properties of the phenylene diamine ; but still it is possible to prepare salts of our substance, if proper precautions are observed, and the chloride is described somewhat later in this paper. Potassic hydrate, even when a boiling concentrated solution was used, produced no effect upon it.

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* Zeitsch. für Chem. 1865, p. 555.

When the tribromphenylene diamine is treated with tin and hydrochloric acid it is converted into phenylene diamine. The details of this work are given later in this paper. The success of this experiment suggested to us that the bromine might be removed also by other reagents ; accordingly we heated some tribromphenylene diamine dissolved in benzol and alcohol with sodic ethylate, the action in one trial being continued for four days, but at the end of this time we recovered nearly the whole of the tribromphenylene diamine taken, and although the filtrate after treatment with nitric acid and argentic nitrate gave a slight precipitate, we ascribe this rather to the complete decomposition of a small portion of the substance (indicated by the dark brown color of the product) than to any simple reaction. As therefore sodic ethylate had no action, it did not seem to us worth while to try other experiments with less energetic reagents.

Chloride of Tribromphenylene Diamine $C_6HBr_3NH_3ClNH_2$. Although the tribromphenylene diamine forms no salts under ordinary conditions, we hoped that we might obtain its chloride by the method which yielded such excellent results to Gattermann * when he applied it to the tribromaniline. Accordingly hydrochloric acid gas was passed into a solution of tribromphenylene diamine in benzol, until it ceased to form a white precipitate, and the liquid fumed strongly. The precipitate was then filtered out, and dried by pressing between filter paper as quickly as possible, after which it was analyzed as follows : — 0.3096 gram of the salt lost 0.0272 gram of hydrochloric acid at 100°.

	Calculated for $C_6HBr_3NH_3ClNH_2$.	Found.
Hydrochloric Acid	9.56	8.79

The residue was entirely free from hydrochloric acid. This result is not so near the theoretical percentage as could be wished, but nevertheless proves that the salt is a monochloride of tribromphenylene diamine. The poor result is undoubtedly to be ascribed to the instability of the compound, which lost as much as 3.3 per cent of its weight from standing four days in a desiccator over sulphuric acid, and therefore might well have lost the 0.77 of one per cent during the drying on filter paper. The chloride as obtained was of a light brown color, although it is probably white when perfectly pure, and as indicated by the description of its analysis is very unstable, decomposing slowly in dry air at ordinary temperatures, quickly and completely when heated to 100°. We should judge that it was somewhat more stable than the chloride of tribromaniline prepared by Gattermann,* as might be expected from the presence of the second amido group. It seems to be soluble in strong hydrochloric acid since the tribromphenylene diamine dissolves in this reagent, but it is decomposed by water.

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* Ber. d. ch. G., XVI. 636.

Tribromphenylene Diacetamide, $C_6HBr_3(NHC_2H_3O)_2$. This substance was made by treating tribromphenylene diamine with acetyl chloride, using anhydrous benzol as a solvent. The action began even in the cold as shown by the deposition of a white precipitate, but to make certain that it was complete the mixture was heated under a return-condenser for one hour. At the end of this time the white sandy precipitate was filtered out, and purified by extraction with glacial acetic acid, followed by recrystallization from the same solvent boiling. It was dried at 100°, and analyzed with the following results: —

I. 0.2726 gram of the substance gave 0.3561 gram of argentic bromide by the method of Carius.

II. 0.2548 gram of substance gave 0.3358 gram of argentic bromide.

	Calculated for $C_6HBr_3(NHC_2H_3O)_2$.	Found.	
		I.	II.
Bromine	55.94	55.59	56.08

Properties. The tribromphenylene diacetamide crytallizes from hot glacial acetic acid in bunches of small white plates much longer than they are broad, which have square ends and frequently radiate from a centre; from alcohol in radiating groups of compound crystals made up of needles united longitudinally. It does not melt at 330°, and is very slightly soluble in all the common solvents. The best solvent for it is hot glacial acetic acid, but it is far from freely soluble even in this.

Tribromphenylene Diurethane, $C_6HBr_3(NHCOOC_2H_5)_2$. Five grams of tribromphenylene diamine were boiled with about twice the amount of chlorocarbonic ester required by the theory in a flask with a return condenser for three hours. The crude product (which weighed 6.5 grams), was purified at first by precipitating the substance with ligroine from its solution in a mixture of benzol and alcohol, afterward by recrystallization from a mixture of alcohol and ligroine, or alcohol and water, until it showed the constant melting point 212,° when it was analyzed with the following results: —

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* Ber. d. ch. G., XVI. 636.

I. 0.3036 gram of the substance gave by the method of Carius 0.3454 gram of argentic bromide.

II. 0.1945 gram of the substance gave 0.2239 gram of argentic bromide.

	Calculated for $C_6HBr_3(NHCOOC_2H_5)_2$.	Found.	
		I.	II.
Bromine	49.08	48.42	48.99

Properties. The tribromphenylene diurethane when deposited from alcohol forms very small crystalline masses, which under the microscope are seen to be rosettes made up of what at first sight appear to be short needles, but on closer examination prove to be groups of finer needles united longitudinally, since they betray their complex nature by the frayed or brushlike appearance of their ends, which resemble a partially untwisted cord. Its color is white, and it melts at 212°. It is soluble in cold alcohol, easily soluble in hot; easily soluble in chloroform, or acetone, less so in ether; somewhat soluble in cold benzol, easily soluble in hot, from which it crystallizes in the same form as from alcohol, but not so well; slightly soluble in carbonic disulphide even when hot; essentially insoluble in ligroine. Water dissolves it to a very slight extent when hot. Hydrochloric acid produced no apparent effect hot or cold; sulphuric acid did not act on it in the cold, but when hot dissolved it; from this solution it seemed to be precipitated unchanged by water, if the heating had not been long continued, but long heating with the strong acid decomposed it. A concentrated solution of potassic hydrate seemed to have no effect on it in the cold, but when heated turned the substance brown, and finally black with apparently complete decomposition. The best solvent for it is alcohol diluted with either water or ligroine.

Reduction of Tribromdinitrobenzol.

Tribromdinitrobenzol (melting at 192°, made from symmetrical tribrombenzol) was reduced by treatment either with zinc and acetic acid, or with tin and hydrochloric acid, but the products were different in the two cases as described in the following sections.

Reduction with Zinc Dust and Acetic Acid. This reduction we found it best to carry on in an atmosphere of carbonic dioxide, as the liquid showed a strong tendency to turn black during the process.

The zinc dust contained in a flask kept full of carbonic dioxide was covered with acetic acid of 80 per cent, and the tribromdinitrobenzol added in small quantities at a time. If the zinc dust and tribromdinitrobenzol were mixed together before adding the acetic acid the action was far too violent; in fact, once the mixture took fire when the acetic acid was added. Even when the process was carried on as directed, the action was energetic at first, but later it was necessary to warm the flask gently to assist the reaction. The products were in part dissolved in the aqueous liquid, which with all our precautions was invariably dark colored, and partly appeared as a crystalline powder in the bottom of the flask. The insoluble part was recrystallized from benzol, by which it was separated into a large fraction melting at 158°, a small amount of substances melting at a lower temperature, and a little unaltered tribromdinitrobenzol. The principal product was shown to be tribromphenylene diamine by its melting point, but to confirm this it was dried at 100° and analyzed, when it gave the following results: —

0.2337 gram of the substance gave by the method of Carius 0.3786 gram of argentic bromide.

	Calculated for $C_6HBr_3(NH_2)_2$.	Found.
Bromine	69.56	68.95

This percentage of bromine, although not agreeing with that calculated so closely as could be wished, is yet accurate enough when taken in connection with the melting point to leave no doubt as to the nature of the substance formed, and therefore we did not attempt to get a number nearer to the theoretical.

The amount of tribromphenylene diamine formed by the reduction was considerable; in one case 10 grams of tribromdinitrobenzol yielded 4.7 grams of it, and 0.9 gram of tribromdinitrobenzol were recovered unaltered, so that the percentage of the theoretical yield was 60.6. The remainder of the product was contained in the aqueous solution (and to a less extent in the small amount of lower melting material from the benzol mother liquors); it undoubtedly consisted of phenylene diamine, from which part or all the bromine had been removed, since the aqueous solution gave tribromphenylene diamine when treated with bromine water, a behavior which, as we have already stated, belongs to solutions of phenylene diamine and its salts.

Reduction with Tin and Hydrochloric Acid. We found it best to proceed as follows: Some granulated tin with a piece of platinum and about 300 c.c. of strong hydrochloric acid were gently warmed in a flask closed by a cork provided with a Bunsen valve, until the greater part of the air had been expelled. 10 grams of tribromdinitrobenzol mixed with enough alcohol to make a thick paste were then added, and the reduction was allowed to go on, warming or cooling the mixture as was necessary, until all the organic substance had dissolved. If the solution thus obtained was a strong one, beautiful white needles of a double tin salt were deposited on cooling; if it was more dilute, they usually appeared after standing a day, but in some cases the substance obstinately refused to crystallize. The crystals were filtered out, and decomposed in concentrated solution with sulphuretted hydrogen, when the filtrate from the sulphide of tin left on evaporation a crystalline solid which after three crystallizations from a mixture of water and hydrochloric acid was analyzed with the following results.

I. 0.2220 gram of the substance gave 31.8 c.c. of nitrogen at a temperature of 26.5° and a pressure of 756.9 mm.

II. 0.2983 gram of the substance gave by the method of Carius 0.4727 gram of argentic chloride.

	Calculated for $C_6H_4(NH_3Cl)_2$.	Found.	
		I.	II.
Nitrogen	15.47	15.79	
Chlorine	39.21		39.17

The tin and hydrochloric acid had therefore reduced both the nitro groups, and also removed all three of the atoms of bromine from the tribromdinitrobenzol; and that the removal of bromine had taken place from the whole of the substance was made probable by the fact that all the organic matter dissolved, whereas the tribromphenylene diamine, as already stated in this paper, is insoluble in water or dilute hydrochloric acid. An additional confirmation of the presence of phenylene diamine was given by the following experiment. The base set free from the soluble chloride analyzed above was treated with bromine water, when a precipitate was formed, which after recrystallization from alcohol containing a little benzol melted at 158°, and was therefore the tribromphenylene diamine which is made in this way from metaphenylene diamine.

When we began work on this subject we made many analyses of the double tin salt which crystallized out of the solution after the reduction; but although in two different preparations we obtained numbers agreeing with the salt $C_6H_4(NH_3ClSnCl_2)_2$ discovered by Gudemann,* we found that in others its composition varied so much that no certain inference in regard to the composition of the base formed could be drawn from these analyses, and therefore prepared the salt free from tin as described above.

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* Zeitsch. für Chem. 1865, p. 51.

After we had shown by the work just described that the three atoms of bromine are removed from tribromdinitrobenzol by tin and hydrochloric acid, it became of interest to determine whether their removal was due to the effect of the two nitro groups upon them. This seemed a probable supposition, because it has been repeatedly observed that atoms of bromine can be easily removed from the benzol ring when they stand in the ortho position to nitro groups, and work done in this laboratory has proved that this tribromdinitrobenzol is a very reactive body, but on the other hand it did not seem likely that the bromine atoms would be removed before the reduction of the nitro groups, as all previous experience seems to show that the latter are much more easily attacked than the former. It was obvious that this point could be decided by trying the action of tin and hydrochloric acid on tribromphenylene diamine, for none of the bromine would be removed from this substance if this action depended on the presence of the nitro groups. Accordingly five grams of tribromphenylene diamine were mixed with tin and hydrochloric acid and a piece of platinum added to increase the action. In the cold no change was observed, and therefore the mixture was warmed on the water bath, when, after a vigorous reaction had gone on for a short time, all the organic matter dissolved. The brown clear solution deposited crystals as it cooled, but disregarding these the whole was treated with an excess of sodic hydrate and extracted with ether repeatedly. The residue from the ethereal extracts was an oil, which solidified after it had been scratched with a sharp glass rod, and then melted at about 62°. There was little doubt therefore that the substance was metaphenylene diamine, which melts at 63°, and this view was confirmed by the following observations. The substance gave a white salt with hydrochloric acid soluble in water, but nearly insoluble in hydrochloric acid. To a solution of this chloride bromine water was added, taking care to avoid an excess ; this produced a white precipitate, which after recrystallization from benzol melted at 158°, and was therefore tribromphenylene diamine. It follows from this experiment (which was repeated several times) that tribromphenylene diamine gives up all its bromine to tin and hydrochloric acid, and therefore that the removal of the bromine atoms does not depend on the loosening effect of the two nitro groups.

Action of Tin and Hydrochloric Acid on Tribrombenzol and on Tribromaniline. After we had shown, as just described, that all the bromine can be removed from tribrommetaphenylene diamine by the action of tin and hydrochloric acid, it occurred to us that the comparatively loose attachment of the bromine to the benzol ring might be due to the fact that the three atoms of bromine were in the symmetrical position, since Blau has shown that one of these atoms in tribrombenzol can be replaced by the methoxy radical, and we have confirmed this observation. This hypothesis seemed the more probable because dibrommetaphenylene diamine is reduced under these conditions much more slowly than the tribrom compound. If this view is correct, tin and hydrochloric acid should remove bromine from the symmetrical tribrombenzol, and accordingly we tried the following experiment. Ten grams of tribrombenzol were mixed with granulated tin and strong hydrochloric acid, a piece of platinum added to promote the action, and enough alcohol to dissolve a large part of the tribrombenzol. The reason for adding the alcohol was that we thought the action of the reducing agent on the tribrommetaphenylene diamine might be in part due to its tendency to dissolve in the acid, or still more to the solubility of the products of the reduction in the acid, and we hoped by the addition of the alcohol to establish similar favorable conditions in the case of the tribrombenzol. The mixture was heated under a return condenser on the water bath for a week. At the end of this time enough water was added to precipitate any brombenzols which might be present, and the heavy crystalline precipitate thus obtained was filtered, and washed until it was free from stannous chloride. It was then dried and weighed, when 9.5 grams were obtained, so that the loss was no greater than would be expected from the rough way in which the experiment had been carried on. This substance melted at 120°, and was therefore unaltered tribrombenzol (melting-point 119.6°). It follows from this experiment that tin and hydrochloric acid do not remove bromine from symmetrical tribrombenzol, and, therefore, that the conversion of tribrommetaphenylene diamine into metaphenylene diamine by these reagents is not due to the symmetrical position of the bromine atoms, although it may have a subsidiary effect in assisting this conversion.

An experiment similar to that just described was tried with 10 grams of tribromaniline. The conditions were exactly the same as those used for tribrombenzol, given at length in the preceding paragraph. Upon adding water to precipitate the organic substances, after the reduction was completed, only a very small precipitate was formed, which in time changed to long needles. This precipitate weighed less than 0.5 gram, and as it melted at 118° was undoubtedly unaltered tribromaniline. The filtrate from this precipitate was treated with an excess of sodic hydrate, the precipitate thus formed dissolved in hydrochloric acid, and reprecipitated with sodic hydrate in excess to remove the hydrates of tin as completely as possible, and then extracted with alcohol. The alcoholic extract deposited long white needles, which melted at 78°–79°, and were therefore probably dibromaniline. To establish the nature of the substance more fully, we tried the following experiments. The amido group was replaced by bromine, when a product was obtained melting at 44°, the melting point of the unsymmetrical tribrombenzol, and this when treated with nitric acid was converted into the mononitrotribrombenzol melting at 93°. There can be no doubt therefore that the tin and hydrochloric acid have removed one of the atoms of bromine from the ortho position to the amido group, replacing it by hydrogen. A quantitative experiment gave the following results, — 10 grams of symmetrical tribromaniline yielded after reduction for six hours 5 grams of dibromaniline, from which were obtained 5 grams of unsymmetrical tribrombenzol, and from this 5.2 grams of tribromnitrobenzol.

Dibrommetaphenylene Dicetamide, $C_6H_2Br_2(NHC_2H_3O)_2$.

Whereas free metaphenylene diamine gives a tribrom derivative, when treated with bromine water, we have obtained only the dibrom compound from metaphenylene diacetamide, even when a considerable excess of bromine was used. The samples analyzed were prepared by the method given below, but a better method discovered later is described after the analyses, — Metaphenylene diacetamide was dissolved in common acetic acid with the aid of gentle heat, and treated at first with bromine, and afterward with bromine water, until a slight excess had been added. The new substance separated from the solution as it was formed, and after standing a short time it was filtered out, and purified by crystallization from hot glacial acetic acid until it showed the constant melting point 259°, when it was dried at 100°, and analyzed with the following results: —

I. 0.2471 gram of the substance gave 19 c.c. of nitrogen at a temperature of 29° and a pressure of 754.3 mm.

II. 0.2145 gram of the substance gave by the method of Carius 0.2294 gram of argentic bromide.

III. 0.2033 gram of the substance gave by the method of Carius 0.2198 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NHC_2H_3O)_2$.	Found. I.	II.	III.
Nitrogen	8.00	8.33		
Bromine	45.71		45.52	46.01

The substance can be obtained more expeditiously in a pure state by avoiding the preparation of solid phenylene diacetamide as follows. A strong ethereal solution of phenylene diamine is treated with acetic anhydride until a portion gives a white or slightly yellow precipitate with bromine (if unaltered phenylene diamine is present, the precipitate will be brown). When this is the case, an excess of bromine water is added to the solution, and the mixture stirred vigorously until the precipitation is complete. The product is essentially pure without recrystallization.

Properties. The dibrommetaphenylene diacetamide crystallizes by slow evaporation from an alcoholic solution in very small, rather short prisms. If on the other hand the crystallization takes place by cooling, obscurely crystalline masses are obtained in which it is hard to make out any definite form; they seem to be prisms coated with needles. Its color is white, and it melts at 259° to 260° with decomposition, as is shown by the fact that the melted mass turns black and puffs up to many times its original volume. On account of this decomposition it is necessary to keep the melting tube in the oil bath as little as possible in determining the melting point. If the substance is allowed to remain in the bath while its temperature is raised, a melting point as low as 250° may be obtained. It is very slightly soluble in cold alcohol, and only a little more soluble in hot; very slightly soluble in benzol, chloroform, or carbonic disulphide; somewhat more soluble in acetone, or glacial acetic acid; essentially insoluble in ether or ligroine. The best solvent for it is glacial acetic acid or alcohol, although it is soluble in the latter only sparingly and with great difficulty. It is very slightly soluble in boiling water, insoluble in cold. Strong hydrochloric acid saponifies it quickly when the two are gently heated together; strong sulphuric acid dissolves it in the cold, but without decomposition, as the unaltered substance is obtained by diluting and neutralizing the acid, it decomposes the substance when hot; if dilute it has no apparent effect when cold, but when heated saponifies and afterward decomposes it; strong nitric acid dissolves it quickly when cold, but the substance is recovered unaltered on neutralization; when hot it decomposes it. A strong solution of potassic hydrate saponifies it when hot.

Dibrommetaphenylene diamine, $C_6H_2Br_2(NH_2)_2$. — This substance was obtained by removing the acetyl groups from the preceding compound as follows: 10 grams of the dibromphenylene diacetamide were heated with from 30 to 40 c.c. of commercial strong hydrochloric acid for half an hour in a flask with a return-condenser; at the end of this time the solid was completely dissolved, and the liquid had taken on a dark brownish red color. After it was cool, the solution was treated at first with sodic carbonate, and finally with sodic hydrate in excess, which precipitated a brown solid. This was filtered out, washed until free from alkali, and purified by crystallization from boiling water containing a little alcohol until it showed the constant melting point 135°. In this recrystallization long heating of the solution should be avoided, as this seems to decompose the substance with precipitation of a black compound. The pure substance was dried at 100° and analysed with the following result: —

0.3872 gram of the substance gave by the method of Carius 0.5473 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NH_2)_2$	Found.
Bromine	60.15	60.16

Properties. — The dibromphenylene diamine crystallizes in fine needles which are white, if the substance is perfectly pure, but usually show a brownish color, which is due to an impurity so slight that it has no effect upon the analysis. It melts at 135°, and is easily soluble in alcohol whether hot or cold. It is very soluble in acetone; easily soluble in ether, somewhat less soluble in benzol, or chloroform, if cold, easily soluble, if hot; slightly soluble in cold carbonic disulphide, soluble when hot; very slightly soluble in cold ligroine, more soluble when it is hot; nearly insoluble in cold water, slightly soluble in hot, but it is decomposed, if boiled for some time with water. The best solvent for it is dilute alcohol. It shows a much stronger tendency to form salts than the tribromdiamine, as it dissolves in either hydrochloric acid or hydrobromic acid, and the solution leaves the salt on spontaneous evaporation; cold strong sulphuric acid turns it purple, and then dissolves it, but upon standing the sulphate separates from this solution in glistening white or pinkish plates, which seem to belong to the monoclinic system; when hot, sulphuric acid decomposes it; strong nitric acid dissolves it, and then decomposes it even in the cold forming a brown solution. A cold solution of potassic hydrate has no effect upon it, but, if the mixture is heated, decomposition sets in as shown by the appearance of a black color. We selected for further study the chloride and the bromide of the base with the results described below.

We have also studied the action of tin and hydrochloric acid on the dibromphenylene diamine. For this purpose 3.75 gram of the dibromphenylene diamine were warmed with tin, hydrochloric acid, and platinum under the conditions already described when speaking of the tribromphenylene diamine. The action in this case was very slow; whereas the tribrom compound dissolved after treatment for a short time, it was necessary to carry on the action for over twelve hours in order to bring the dibromamine into solution. The product yielded an oily free base, smelling like metaphenylene diamine, which, however, we did not succeed in obtaining in a solid state. It gave an easily soluble chloride, so there can be no doubt that bromine was removed. We are unable to determine with certainty the cause of the very slow removal of the bromine from the dibromphenylene diamine; it is possible that it is only mechanical, as it was observed that this substance showed a tendency to form a coating on the surface of the tin, or on the other hand it may be that the symmetrical position of the three atoms of bromine in the tribromphenylene diamine has the effect of loosening their attraction for the benzol ring. This latter explanation seems to us the more probable.

Chloride of Dibromphenylene Diamine, $C_6H_2Br_2NH_3ClNH_2$. This salt can be made by dissolving the diamine in strong aqueous hydrochloric acid and allowing the solution to evaporate spontaneously, but we did not use this method in preparing the salt for analysis, because we feared that it might undergo a partial decomposition, if deposited from a solution containing water. We therefore prepared it by passing hydrochloric acid gas through a solution of the diamine in benzol, until the liquid fumed strongly, and no more solid matter was deposited. The precipitate thus obtained was pressed repeatedly between filter paper, and dried for one hour over sulphuric acid, when it gave the following result on analysis: —

0.2173 gram of the salt gave by the method of Carius 0.3713 gram of the mixture of argentic chloride and bromide.

	Calculated for $C_6H_2Br_2NH_3ClNH_2$	Found.
Chlorine and Bromine	64.63	64.28

The chloride of dibromphenylene diamine is much more stable than the corresponding tribrom-compound, since, whereas the chloride of tribromphenylene diamine lost all its hydrochloric acid when heated to 100° for a short time, the chloride of dibromphenylene diamine showed a loss under the same conditions of only 5 per cent instead of the 12.07 per cent, which represents the loss, if the whole of its hydrochloric acid had been given up. Further the salt of the dibrom compound can be made by the action of a strong aqueous solution of hydrochloric acid upon the free base, while, although the tribrom base dissolves in strong hydrochloric acid, we have not succeeded in obtaining the solid chloride from this solution. It must not be inferred from this comparison, however, that the chloride of dibromphenylene diamine is especially stable, for this is not the case, since it loses nearly 4 per cent of its weight by standing in a desiccator, and is also decomposed by water.

Bromide of Dibromphenylene Diamine, $C_6H_2Br_2NH_3BrNH_2$. — This substance was made by adding dibromphenylene diamine to distilled hydrobromic acid (boiling point 123°) until it ceased to dissolve easily in the cold. A good deal of trouble was encountered in obtaining the solid salt from this solution, as heating decomposed it, and none of the organic solvents miscible with water gave a precipitate with it; spontaneous evaporation indeed gave the salt, but as we did not know its properties at the time of the preparation we were afraid of decomposition during such long standing, and accordingly proceeded as follows: The aqueous solution was covered with a rather thick layer of ether, and the whole stirred vigorously for about a quarter of an hour; under this treatment the bromide crystallized out in the lower part of the ether, when it was separated, washed with ether, and dried in a desiccator over sulphuric acid. It then gave the following results on analysis: —

I. 0.4433 gram of the substance gave by the method of Carius 0.7191 gram of argentic bromide.

II. 0.3014 gram of the substance gave 0.4884 gram of argentic bromide.

	Calculated for $C_6H_2Br_2NH_3BrNH_2$	Found. I.	II.
Bromine	69.16	69.04	68.96

The sample used in the first analysis had been dried for only three hours, that for the second had stood in a desiccator over sulphuric acid for three days, showing that the salt is stable under these circumstances. The bromide is therefore more stable than the chloride, as that lost nearly four per cent of its weight in a desiccator, which amounts to one third of the acid that it contains.

The bromide of dibromphenylene diamine forms white needles, which turn brown quickly, when exposed to the air. It is decomposed by water, but is soluble in ethyl, or methyl alcohol, the solution apparently decomposing on standing; insoluble in ether, benzol, or ligroine.

Reduction of Tetrabromdinitrobenzol. The tetrabromdinitrobenzol was prepared essentially by the method given by Bancroft and one of us,* but a few improvements in the process should be mentioned here. By using a large amount of glacial acetic acid the yield of tetrabrombenzol was materially raised. The details of this process will be found in our paper, "On the Behavior of Certain Halogen Derivatives of Benzol." In converting the tetrabrombenzol into the dinitro compound we found that the quantities of sulphuric acid and nitric acid used could be reduced to 50 c.c. of each for 10 grams of tetrabrombenzol, if the tetrabrombenzol was pure; if this was not the case the best method was to treat the tetrabrombenzol with the acid mixture, which had already been used once with tetrabrombenzol; the product of this action of the residual acid was then treated with one half the amount of fresh sulphuric acid and nitric acid needed for the complete conversion of the tetrabrombenzol into the dinitro compound, and in this way a nearly pure product was obtained at little expense of fuming nitric acid. With pure tetrabrombenzol the yield was very nearly quantitative, 100 grams giving 121 grams of a product melting at 220°, which after one recrystallization melted at 227°, the correct melting point for tetrabromdinitrobenzol; as 100 grams should give 122.8 grams, this makes the yield of this crude product over 99 per cent.

To reduce the tetrabromdinitrobenzol it was mixed with alcohol, tin, and hydrochloric acid, and the mixture heated on the water bath in a flask with a return condenser, more hydrochloric acid being added from time to time. When the volume of liquid became unpleasantly large, it was evaporated in an open dish to a convenient volume, and returned to the flask with fresh alcohol and acid. After the organic matter had gone completely into solution, which usually happened after boiling for about 70 hours, the liquid was again concentrated and rendered strongly alkaline with crude sodic hydrate. The hydrate of tin was filtered out with cheese cloth, and dried as thoroughly as possible by sucking air through it, after which it was shaken repeatedly with rather large amounts of alcohol. The alcoholic extract thus obtained was freed from alcohol by distillation, followed by evaporation on the water bath, when an oil and an aqueous solution were left, which were separated, if possible, mechanically; if not, by shaking with ether. The oil obtained directly or from the ether solidified after a short time. The aqueous filtrate from the hydrate of tin with the liquid separated from the oil was shaken with ether repeatedly, and the oil thus obtained added to the main portion. The aqueous solution after shaking with ether gave a very slight precipitate on the addition of bromine, but the amount of tetrabromphenylene diamine obtained in this way was so small that this treatment is hardly worth while. The principal product, after it had solidified, was purified by dissolving is in rather dilute alcohol and saturating the solution with suphuretted hydrogen, when it was warmed gently, and allowed to stand in a corked flask for some time; after filtering off the sulphide of tin it was evaporated to dryness, and the residue recrystallized from pure ligroine (boiling from 60°–70°) until it showed the constant melting point 93°–94°, when it was dried in a desiccator and analyzed with the following result: —

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* These Proceedings, XXIV. 289.

0.2117 gram of the base gave by the method of Carius 0.2113 gram of argentic bromide.

	Calculated for $C_6H_3Br(NH_2)_2$.	Found.
Bromine	42.79	42.48

Properties of Monobrommetaphenylene Diamine. It crystallizes from a mixture of benzol and ligroine in white spindle-shaped forms often a centimeter long; from benzol alone in bundles of small needles united longitudinally; from alcohol in not very well developed prisms apparently belonging to the monoclinic system and often twinned. It melts at 93°–94°, and is readily soluble in acetone, alcohol, ether, or chloroform; in benzol, or carbonic disulphide it is slightly soluble in the cold, more freely when hot; nearly insoluble in cold ligroine, difficultly soluble in hot; it is moderately soluble in cold water, as shown by the fact that such a solution gives a good precipitate with bromine water; in hot water it is even more soluble, the solution as it cools depositing oil drops, which later change to needles. The best solvent for it is a mixture of benzol and ligroine, but crystallization from pure ligroine is necessary to get a perfectly white product. It shows a tendency to separate from its solutions at first as an oil, and also to become decomposed, when in solution, forming a brown product.

The monobromphenylene diamine shows marked basic properties. Hydrochloric acid or hydrobromic acid gives with it a salt soluble in water, a description and analysis of the bromide formed in this way is given below; moderately strong sulphuric acid also gives a soluble salt, which forms white crystals when the solution is allowed to evaporate spontaneously; dilute nitric acid seems to have little action on it in the cold, but when hot converted it into a brown substance. Sodic hydrate seemed to have no action even when warmed with it for several minutes on the water bath. The constitution of this monobromphenylene diamine is probably NH_2. H. NH_2. H. Br. H, as the tribromdinitrobenzol made from symmetrical tribrombenzol loses all its bromine when reduced under the conditions used in obtaining the monobromphenylene diamine from tetrabromdinitrobenzol.

Bromide of Monobromphenylene Diamine, $C_6H_3Br(NH_3Br)_2$.

Monobromphenylene diamine was mixed with distilled hydrobromic acid (boiling point 124°–125°), and the liquid heated to boiling. The solid was then brought into solution by the careful addition of just the proper amount of water to the boiling solution, after which more of the hydrobromic acid was added, until crystallization began, when the mixture was allowed to cool; the crystals thus obtained were washed with hydrobromic acid and then with ether, dried by pressure with filter paper, and washed with ether a second time. After drying over sulphuric acid the salt was analyzed with the following result: —

0.2474 gram of the substance gave according to the method of Carius 0.3945 gram of argentic bromide.

	Calculated for $C_6H_3Br(NH_3Br)_2$.	Found.
Bromine	68.77	67.86

This analysis leaves much to be desired, but the result is near enough to show that the formula given above is correct. The salt forms colorless transparent glassy crystals, which look like cubes under the microscope; freely soluble in water, slightly in hydrobromic acid.

Tetrabromphenylene Diamine, $C_6Br_4(NH_2)_2$.

This substance was made by dissolving the monobromphenylene diamine, melting at 93°–94° in ether and adding a slight excess of bromine; the product, after recrystallization from a mixture of chloroform and ligroine, showed the constant melting point 212°–213°, when it was dried and analyzed with the following result: —

I. 0.2357 gram of the substance gave by the method of Carius 0.4166 gram of argentic bromide.

II. 0.2493 gram of the substance gave 0.4432 gram of argentic bromide.

	Calculated for $C_6Br_4(NH_2)_2$.	Found.	
		I.	II.
Bromine	75.47	75.22	75.67

Properties of Tetrabromphenylene Diamine. It crystallizes in very small white needles, which melt at 212°–213°, and are freely soluble in benzol, chloroform, ether, acetone, or carbonic disulphide; slightly soluble in cold alcohol, freely in hot; almost insoluble in cold ligroine, slightly soluble in hot. The best solvent for it is a mixture of chloroform or benzol with ligroine. The tetrabromphenylene diamine has nearly, if not quite, lost the basic properties of a diamine, as was to be expected since it is loaded with so many negative bromine atoms. Hydrobromic acid had but little apparent action on it, even when hot, although the liquid deposited after long standing a few transparent crystals, which may have been the bromide.